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15 TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON  
CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME

20 BACKGROUND OF THE INVENTION

20 Field of the Invention

This invention relates to transparent conductive oxide (TCO) films or coatings, and in particular to new multi-cation, thin film, n-type TCO films in which optimal electron 25 concentration and mobility is achieved by selecting dopants having ionic sizes that approximate those of the oxide host material, and therefore are essentially non-disruptive to the host crystal lattice, thereby reducing electron scattering and increasing film conductivity.

- 30 The invention also relates to a method of forming TCO films or coatings by atmospheric pressure chemical vapor deposition (APCVD) of soluble solutions with a controlled crystallite size, quality and orientation to yield new n- type TCOs with enhanced electron concentration and mobility, and minimal defects.
- 35 The improved TCO films of the invention may be used in a variety of applications where performance of the films is affected by electron concentration and/or electron mobility, including solar control films in applications requiring a low plasma wavelength, and

ohmic contact films in applications where low-resistivity is critical, such as in wide band gap semiconductor devices.

#### Description of Related Art

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One of the applications of the TCO films or coatings of the invention is for use as solar control coatings, such as might be used on window glass. In general, it is desirable for such coatings to maximize transmittance of visible light while reflecting most infrared and near infrared (NIR) light. The amount of NIR light reflected depends on the 10 “plasma wavelength,” which in a TCO coating or film is inversely proportional to the electron concentration in the coating. On the other hand, the transmittance of visible light by a TCO coating depends on electron mobility. In order to achieve an effective solar control coating, it is necessary to have a low plasma wavelength (or high plasma frequency), and high electron mobility. However, current thin film coating technologies 15 permit only one of the two desired properties, electron concentration and electron mobility, to be optimized in a given film.

Much of the present research on thin film TCOs has focused on increasing conductivities, particularly with respect to Indium and/or Cadmium cation combinations. See, e.g., A.J. 20 Freeman et al., MRS Bulletin, August 2000, pp. 45-51. However, even though In-Cd-O phases have some of the highest room temperature electrical conductivities measured for thin films (3500 S/cm), with mobilities as high as 200 cm<sup>2</sup>/Vs, electron concentrations were only  $1 \times 10^{20}$  e/cm<sup>3</sup>, well below the typical  $10^{21}$  for doped In<sub>2</sub>O<sub>3</sub> films. On the other hand, some highly conductive In-Ga-Sn-O phases have conductivities as high as 3280 25 S/cm with measured electron concentrations of  $8.6 \times 10^{20}$  e/cm<sup>3</sup>, but mobilities of only 24 cm<sup>2</sup>/Vs. Thus, in these prior art materials, either the electron concentration is too low to achieve an optimal plasma wavelength, or the electron mobility is too low to achieve optimal transmittance.

30 Most of the prior films were prepared using low pressure and plasma assisted chemical vapor deposition (CVD), and/or dc or rf sputtering techniques, as opposed to APCVD, as

discussed above. Examples of currently used TCOs deposited by sputtering on glass include ZnO:Al, Cd<sub>2</sub>SnO<sub>4</sub>, Zn<sub>2</sub>SnO<sub>4</sub>, ZnSnO<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, WO<sub>3</sub>, and RuO<sub>2</sub>. Examples of currently used TCOs which may be deposited by conventional low pressure CVD include ZnO:In(Al, F, Ga), SnO<sub>2</sub>:F, TiN, and In<sub>2</sub>O<sub>3</sub>:Sn (ITO). A preferred commercial thin film  
5 TCO coating material, In<sub>2</sub>O<sub>3</sub>:Sn, has a plasma wavelength of 1 mm with an electron concentration of 10<sup>21</sup> cm<sup>-3</sup>.

One approach to increasing the conductivity of TCO films by using APCVD, as opposed to conventional low pressure CVD or sputtering, is described in U.S. Patent No.  
10 6,524,647 (Varanasi et al.), which discloses APCVD of niobium doped tin oxide films. According to the Varanesi et al. patent, niobium is especially suited for replacing tin in the tin oxide lattice because it has a similar outer shell electron configuration and a comparable atomic number to that of tin. However, Varanesi et al. fails to optimize electrical properties because it fails to recognize that a key factor is actually the ionic size  
15 of the dopant, rather than atomic number or outer shell electron configuration.

In contrast, the present invention seeks to enable the ideal balance between electron concentrations, by selection of dopants according to the ionic size of the dopant relative to the oxide matrix, and appropriate control of the APCVD process used to deposit the  
20 doped oxides. None of the above-mentioned processes takes into account ionic size for the purpose of optimizing electron concentration and/or electron mobility.

## SUMMARY OF THE INVENTION

25 It is accordingly a first objective of the invention to overcome the disadvantages of the prior art by providing TCO films having improved electrical properties, and that can be produced in an efficient and cost-effective manner.

It is a second objective of the invention to provide TCOs having high visible transmission  
30 and improved NIR reflective properties.

It is a third objective of the invention to provide transparent conductive oxides having high conductivity and an optimal combination of electron concentration and electron mobility for a given application.

- 5 It is a fourth objective of the invention to provide a method of making transparent conductive oxides that permits optimization of electron concentration and electron mobility, in order to improve visible transmission and NIR reflective properties, and/or to provide films having low resistivity and high work function.
- 10 It is a fifth objective of the invention to provide a method of using APCVD to deposit TCO films or coatings having improved electrical or optical properties.

These objectives of the invention are accomplished, in accordance with the principles of a preferred embodiment of the invention, by a variety of new n-type TCO films in which 15 the dopants have ionic sizes that approximate those of the metal oxide host material, and that therefore are essentially non-disruptive to the host crystal lattice, reducing electron scattering and increasing film conductivity.

These objectives are further achieved by using atmospheric pressure chemical vapor 20 deposition to deposit soluble solutions having ionic sizes that approximate those of the metal oxide host material to be deposited. The resulting doped metal oxide films have higher conductivities, which in turn imparts better NIR reflective properties to the films than, for example, the current state of the art tin doped indium oxide.

25 According to a first preferred embodiment of the invention, a metal oxide host, is deposited on a substrate in conventional fashion, but the dopants are chosen to approximately match the ionic size of the host crystals. Suitable hosts, with ionic size given in parentheses, include  $Zn^{2+}(0.74\text{\AA})O$ ,  $Sn^{4+}(0.71\text{\AA})O_2$ ,  $Ge^{4+}(0.53\text{\AA})O_2$ ,  $Zr^{4+}(0.80\text{\AA})O_2$ ,  $Ti^{4+}(0.68\text{\AA})O_2$ , or  $Ga^{3+}(0.62\text{\AA})_2O_3$ , while suitable dopants according to 30 the invention include ions such as  $Sn^{4+}(0.71)$ ,  $Bi^{5+}(0.74\text{\AA})$ ,  $Ta^{5+}(0.73\text{\AA})$ ,  $Hf^{4+}(0.80\text{\AA})$ ,  $Mo^{6+}(0.62\text{\AA})$ ,  $Te^{6+}(0.59\text{\AA})$ ,  $Nb^{5+}(0.70\text{\AA})$  and the like, all of which have sizes that

approximate those of the metal oxide host material. The enhanced conductivity is manifest by both an increase of electron concentration and mobility as measured by the Hall effect.

5 According to a second preferred embodiment of the invention, a rutile MO<sub>2</sub> layer is deposited on SnO<sub>2</sub> or other metal oxide capable of stabilizing the rutile MO<sub>2</sub> film and optimize near infrared (NIR) reflection in glass/SnO<sub>2</sub>/MO<sub>2</sub> bilayers and glass/SnO<sub>2</sub>/MO<sub>2</sub>/SnO<sub>2</sub> sandwich structures. Suitable rutile MO<sub>2</sub> materials include but are not limited to M = Ti, V, Cr, Mo, Ru, or mixed alloys thereof.

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According to a third preferred embodiment of the invention, Sn<sub>x</sub>M<sub>1-x</sub>O<sub>2</sub> films are deposited on a substrate, where the metal- semiconductor transition of MO<sub>2</sub> films is modified by alloying with SnO<sub>2</sub>, thus optimizing the NIR reflection.

15 According to a fourth preferred embodiment of the invention, films such as but not limited to WO<sub>3</sub>, Mo<sub>x</sub>O<sub>y</sub>, A<sub>x</sub>WO<sub>3</sub>, and A<sub>x</sub>Mo<sub>1-x</sub>O<sub>y</sub> are deposited on a substrate where A is H, Li, Na, and K, and x = 0-2 and high enough to modify the plasma wavelength to optimize the NIR reflectance. The film properties may be enhanced by APCVD deposition of WO<sub>3</sub> or Mo<sub>x</sub>O<sub>y</sub> on soda lime glass substrates with consecutive  
20 annealing/diffusion of Na, Li and K from the glass, and/or vapor phase incorporation/implantation of A into WO<sub>3</sub>.

Electron concentrations ranging from 7-10x10<sup>20</sup>e/cm<sup>3</sup> are possible with the novel n-type TCO films deposited by the above-described processes, as well as electron mobilities of  
25 50-150 cm<sup>2</sup>/vsec. In addition, these doped metal oxide films can be undercoated with one or more functional layers that can act as barrier layers to ion migration from the glass, anti-iridescent layers to reduce reflected color, and/or nucleation layers to alter the orientation of the TCO layer(s).

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#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As will be apparent from the examples set forth below, this invention provides a variety of new n-type TCO films, each having an ideal balance between electron concentration and mobility, by selecting dopants that are essentially non-disruptive to the host crystal lattice, thereby reducing electron scattering and increasing film conductivity. According to the method of the invention, the films are deposited on heated substrates such as glass by APCVD of organometallic precursors combined with specific dopants and other additives such that the deposited films have a higher electron concentration. The higher electron concentration is due to the incorporation of dopant ions in the host oxide lattice that cause little or no disruption of the lattice parameters, thereby decreasing electron scattering and increasing conductivity.

In a first preferred embodiment of the invention, doped metal oxide films are prepared by APCVD on a suitable substrate, such as soda lime glass, the metal oxides having crystal lattice host sizes ranging from .60Å to .80Å. Therefore, according to the principles of the invention, the ionic sizes of the dopants are also chosen to be approximately within this range. For example, suitable metal oxide hosts include, but are not limited to,  $Zn^{2+}(0.74\text{\AA})O$ ,  $Sn^{4+}(0.71\text{\AA})O_2$ ,  $Ge^{4+}(0.53\text{\AA})O_2$ ,  $Zr^{4+}(0.80\text{\AA})O_2$ ,  $Ti^{4+}(0.68\text{\AA})O_2$ , and  $Ga^{3+}(0.62\text{\AA})_2O_3$ , the ionic sizes of which are set forth in the parentheses. Ideal dopants for these metal oxide hosts include ions such as  $Sn^{4+}(0.71)$ ,  $Bi^{5+}(0.74\text{\AA})$ ,  $Ta^{5+}(0.73\text{\AA})$ ,  $Hf^{4+}(0.80\text{\AA})$ ,  $Mo^{6+}(0.62\text{\AA})$ ,  $Te^{6+}(0.56\text{\AA})$ ,  $Nb^{5+}(0.70\text{\AA})$  and the like, as well as combinations of any of the above-dopants.

Table 1 is a table illustrating the properties of  $MO_2$  compounds with rutile structure manufactured according to the principles of the first preferred embodiment of the invention.

Table 1.  $\text{MO}_2$  compound properties with rutile structure

$\text{MO}_2$	a, Å	c, Å	$V \sim 10^{-23} \text{ cm}^{-3}$	$N_{\text{Site}}(\text{Sn}) \sim 10^{22}, \text{ cm}^{-3}$	$N_{\text{Site}}(\text{O}) \sim 10^{22}, \text{ cm}^{-3}$	% dopant (O)*	$E_G, \text{ eV}$	Thermal Expansion	Plasma $\sim_p, \text{ m}$
$\text{SnO}_2$	4.738	3.187	7.115	2.8	5.6	3.57	3.8	0.02	1.3 ( $7 \sim 10^{20} \text{ cm}^{-3}$ )
$\text{TiO}_2$	4.585	2.95	6.2	3.22	6.45	3.1	3.0	0.114	
$\text{MnO}_2$	4.396	2.871	5.548	3.6	7.2	2.7	Metal	0.05	

5 \* - the required incorporation of a singly charged donor F, Cl, Br on O lattice site to obtain  $n = 2 \sim 10^{21}, \text{ cm}^{-3}$  with the plasma wavelength of  $0.77 \sim \text{m}$ .

In a second preferred embodiment of the invention, the principles of the invention are applied to hetero-epitaxial growth of APCVD-deposited doped and undoped rutile  $\text{MO}_2$  structures, where M = Ti, V, Cr, Mo, Ru or mixed alloys thereof, on a  $\text{SnO}_2$  or other metal oxide layer suitable for stabilizing the rutile  $\text{MO}_2$  film and optimizing the near infrared reflection (NIR) in glass/ $\text{SnO}_2/\text{MO}_2$  bilayers and glass/ $\text{SnO}_2/\text{MO}_2/\text{SnO}_2$  sandwich structures. Some of the  $\text{MO}_2$  materials, such as  $\text{CrO}_2$ ,  $\text{MoO}_2$ ,  $\text{RuO}_2$ , have metallic conduction with high visible absorption. Others, such as  $\text{TiO}_2$ , are semiconductors with band gaps of 3.0 eV and high visible transparency. Still others, such as  $\text{VO}_2$ , have metal to semiconductor transitions at 340K. In all cases, however, the invention permits modification of the NIR reflectance of the coatings by depositing glass/ $\text{SnO}_2/\text{MO}_2$  bilayers and glass/ $\text{SnO}_2/\text{MO}_2/\text{SnO}_2$  sandwich structures, where other metal oxides capable of stabilizing the rutile  $\text{MO}_2$  layer may be substituted for  $\text{SnO}_2$ .  
 10 Since the host materials crystallize in a rutile structure, as illustrated in Fig. 1, it is expected that the deposited  $\text{MO}_2$  films will crystallize in a similar fashion to produce epitaxial like layers. Also, since lattice parameters are close to that of  $\text{SnO}_2$  for most of these materials, only small stresses are expected in (001) planes.  
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 25 The third preferred embodiment of the invention involves a variation of the second preferred embodiment in which APCVD is used to grow  $\text{Sn}_x\text{M}_{1-x}\text{O}_2$  ternary alloy system layers that modify the band gap parameters of  $\text{SnO}_2$ . By tuning the fraction of the

transition metal, one can obtain the necessary high NIR reflection with high electron concentration.

Finally, in accordance with the principles of a fourth preferred embodiment of the invention, APCVD is used to grow oxide coatings having the form  $\text{WO}_3$  (as well as oxides such as  $\text{Mo}_x\text{O}_y$ ) and  $\text{A}_x\text{WO}_3$ , ( $\text{A}_x\text{Mo}_{1-x}\text{O}_y$ ), where A is H, Li, Na, and K, and x = 0-2 and high enough to modify the plasma wavelength to optimize the NIR reflectance. In one embodiment, enhanced film properties are achieved by APCVD deposition of  $\text{WO}_3$  or  $\text{Mo}_x\text{O}_y$  films on soda lime glass substrates with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase incorporation/implantation of A into  $\text{WO}_3$ .

Theoretical studies of  $\text{A}_x\text{WO}_3$  indicate the possibility of a reflectance band shift towards the visible by increasing the fraction x of alkali metals in the ternary compound.

According to a preferred embodiment of the invention, the plasma wavelength of these coatings is tuned to 0.7 mm by varying the content of alkali metals in the coatings on glass and other substrates. Note that the amount of A is significantly higher than that used in Li-doped  $\text{WO}_3$  films prepared for their electrochromic properties, where alkali doping is typically less than a few percent. In addition, one can use Na (Li, K) diffusion from glass substrates in APCVD grown  $\text{MO}_y$  films to help promote formation of  $\text{A}_x\text{MO}_3$ . In addition, implantation or vapor deposition of films with A may be used in this embodiment.

A predictive example of the first preferred embodiment of the invention, in which the doped metal oxide is tantalum doped zinc oxide, follows:

#### Predictive Example

A 2.2 mm thick glass substrate (soda lime silica), two inches square, is heated on a hot block to about 650°C. The substrate may be positioned about 25 mm under the center section of a vertical concentric tube coating nozzle. A carrier gas of dry oxygen flowing

at a rate of 12.5 liters per minute (lpm) is then heated to about 160°C and passed through a hot wall vertical vaporizer.

A liquid coating solution containing monobutyltin trichloride (MBTC) is fed to the  
5 vaporizer via a syringe pump at a volume flow designed to give a 0.5 mol % concentration in the gas composition. A second liquid coating solution of tetraethyl orthosilicate (TEOS) and triethyl phosphite (TEP) in a 1:1 mol ratio is fed to the vaporizer via a syringe pump at a volume flow designed to give a 0.5 mol % concentration in the gas composition.

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The gas mixture is then allowed to impinge on the glass substrate for about 4 seconds to deposit a mixed oxide of tin and silicon about 80 nm thick with a refractive index of about 1.70. Immediately following, a second gas mixture composed of a diethylzinc tetraethylethylenediamine complex (DEED), a nitrogen carrier gas, tantalum (V)  
15 ethoxide, water vapor and air is caused to impinge on the metal oxide coated surface for about 30 seconds, resulting in a tantalum doped zinc oxide film of about 300 nm. The second gas mixture may be formed by mixing separate gas streams in a manifold just before the coating nozzle. The water vapor and air are introduced at the top of the nozzle to minimize premature reaction with the zinc and tantalum precursors. The DEED liquid  
20 is fed via a syringe pump to a second vaporizer through which a nitrogen carrier gas is flowing at 160° C at about 10 lpm. The volume flow is preferably designed to give a 0.5 mole % concentration in the carrier gas.

Finally, the tantalum precursor is fed via a syringe pump to a third vaporizer through  
25 which a nitrogen carrier gas is flowing at 180° C at about 10 lpm. The volume flow is designed to give a 0.1 mole % concentration in the carrier gas. Water is fed via syringe pump into a vaporizer through which an air carrier gas was flowing at about 10 lpm. The vapor concentration is about 3 moles per mole of zinc precursor.

30 The bilayer film stack made by the above method is predicted to have essentially no reflected color, a visible transmission greater than 70 %, an electron concentration in the

range of  $7\text{-}10 \times 10^{20} \text{ e/cm}^3$  and a mobility above  $50 \text{ cm}^2/\text{v}\cdot\text{sec}$  as measured by the Hall effect.

In a similar manner, hafnium doped zirconium dioxide, molybdenum doped gallium oxide and bismuth/tantalum doped tin oxide films could be prepared. In some cases, the precursors would be placed in heated bubblers and the carrier gas would pass through a molten liquid. These examples are only illustrative of the current invention and one skilled in the art will realize that minor variations outside these embodiments do not depart from the spirit and scope of this invention.

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Having thus described various preferred embodiments of the invention in sufficient detail to enable those skilled in the art to make and use the invention, it will nevertheless be appreciated that numerous variations and modifications of the illustrated embodiment may be made without departing from the spirit of the invention. For example, other dopant and host combinations not mentioned herein could be used. Binary and tertiary dopant combinations could be found which might yield films with even higher conductivities. Other undercoat films could be used which have better barrier, anti-reflection or nucleating layer properties than the combinations described herein. Anti-reflection layers could be placed on top of the doped metal oxide layer. Dopants could be incorporated into the host oxide layer in a gradient fashion; one dopant gradually decreasing while the other gradually increases in a continuum or step fashion. Separate dopant layers could be combined. The dopants described herein all are intended to replace some of the metal host ions. The enhanced effect might also be accomplished by combining dopants of this invention with dopants such as fluorine that substitute for some of the oxygen atoms in the host matrix.

As a result, it is intended that the invention not be limited by the above description, but that it be defined solely in accordance with the appended claims.